

PATENT ABSTRACTS OF JAPAN

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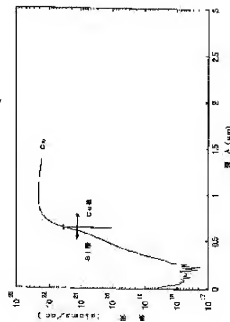
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(54) SECONDARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To restrain pulverization of active material particles and also improve cycle performance of a secondary cell which employs electrodes including the active material particles alloying with Li.

SOLUTION: This active material particle of the electrode has a diffusively distributed metallic element which does not alloy with Li.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a rechargeable battery.

It is related with the rechargeable battery using Li and the active material particle to alloy as an active material in detail.

[0002]

[Description of the Prior Art]Since the energy density is large, the lithium secondary battery using the lithium metal as a negative electrode attracts attention as a next-generation rechargeable battery. However, in order to use a lithium metal for a negative electrode, a dissolution deposit of a lithium metal arises in connection with charge and discharge, and generation of a dendrite and modification of an electrode arise. For this reason, what cycle performance is inferior and can be equal to utilization is not made. As what can solve such a problem, Li alloy negative electrode using Li and the metal to alloy and the carbon negative electrode using carbon materials, such as black lead, are proposed, and a part of thing using a carbon negative electrode is put in practical use.

[0003]

[Problem(s) to be Solved by the Invention]However, since the theoretical capacity of a carbon negative electrode is as low as 372 mAh/g, there is a fault that an energy density falls substantially, compared with the case where metal lithium is used for a negative electrode. Since expansion and contraction of volume were repeated in connection with charge and discharge when Li alloy negative electrode is used, the active material particle carried out pulverization as the charging and discharging cycle progressed, and there was a fault that cycle performance worsened.

[0004]In the rechargeable battery using the electrode containing Li and the active material particle to alloy, the purpose of this invention can control the pulverization of an active material particle, and there is in providing the rechargeable battery which can raise cycle performance by leaps and bounds.

[0005]

[Means for Solving the Problem]A rechargeable battery of this invention is a rechargeable battery using an electrode containing Li and an active material particle to alloy, and is characterized by Li and a metallic element which is not alloyed carrying out diffusion distribution into an active material particle.

[0006]In the 1st aspect of affairs of following this invention, concentration of Li and a metallic element which is not alloyed is characterized by increasing as it goes to the surface from an inside of an active material particle.

[0007]In the 2nd aspect of affairs of following this invention, concentration of Li and a metallic element which is not alloyed is characterized by decreasing as it goes to the surface from an inside of an active material particle.

[0008]In this invention, especially if Li and an active material particle to alloy are formed from Li and material to alloy, they are not limited, but from a viewpoint of obtaining big electrode capacitance, it is desirable that they are at least one or more sorts chosen from Si, germanium, Sn, aluminum, and In. Since theoretical capacity is large, especially Si is used preferably.

[0009]In this invention, especially if Li which carries out diffusion distribution into an active material particle, and a metallic element which is not alloyed are Li and a metallic element which is not alloyed, it is not limited, but it is preferred that it is a material excellent in conductivity, and Cu is preferably used especially from such a viewpoint.

[0010]Therefore, in a desirable embodiment according to this invention, an active material particle consists of Si substantially, and it is characterized by a metallic element being Cu. Although an active material particle in

this invention can be used also as any of negative electrode active material and positive active material, since standard potential to a lithium metal of Li and an active material to alloy is generally low, it thinks [being used as negative electrode active material in many cases, and].

[0011](Operation effect) Generally, an electrode active material binds a powdered active material with a binder, and is produced. Therefore, the powder as an active material itself serves as a place of an electrode reaction. When occlusion of the Li is carried out to a powdered active material, Li enters from the powder surface first. Generally, if Li goes into an active material and is alloyed, since the volume expands, the powdered surface will expand, but since Li is not contained, an inside does not expand. Therefore, the rates of expansion in the surface and an inside differ greatly, and powder breaks and carries out pulverization. Pulverization can be controlled by adjusting a difference of the rate of expansion of this surface and an inside. In this invention, by carrying out diffusion distribution of Li and the metallic element which is not alloyed into an active material particle, a difference of the rate of expansion of such the surface and an inside was made small, and pulverization is controlled.

[0012]In the 1st aspect of affairs of this invention, Li and a metallic element which is not alloyed have the concentration distribution which increases as it goes to the surface from an inside of an active material particle. In such a case, on the surface, concentration of Li and a metallic element which is not alloyed is high, since concentration of an active material is low, even if it carries out occlusion of the Li, the surface rate of expansion is small, and what has so large a difference of the rate of expansion with an inside to which occlusion of the Li is not carried out does not become. Therefore, internal stress becomes small and a crack of an active material particle can be controlled.

[0013]In the 2nd aspect of affairs of this invention, the above-mentioned metallic element has the concentration distribution which decreases as it goes to the surface from an inside of an active material particle. In such a case, since active material concentration of a particle surface is high, expansion of the surface is large, expansion of an inside becomes small, and internal stress becomes large. However, inside particles, since active material concentration is low, an inside of a particle does not reach but a crack generated in a particle surface will be in the state where only a particle surface broke. As a result, pulverization is not carried out as the whole particle, but it will be in the state where pulverization was controlled.

[0014]Although various methods can be considered as a method of producing an active material particle which is increasing as concentration of Li and a metallic element which is not alloyed goes to the surface from an inside of an active material particle according to the 1st aspect of affairs of this invention, the following methods are mentioned, for example.

[0015]** How to heat-treat at a suitable temperature and to make an inside diffuse a metallic element from the surface of an active material particle after providing a layer of Li and a metallic element which is not alloyed by electroless plating on the surface of Li and an active material particle to alloy.

[0016]When Cu is used as a metallic element, using Si powder as Li and an active material particle to alloy, After forming a Cu layer by electroless plating on the surface of Si powder, it heat-treats and Cu is diffused in Si powder, and concentration distribution which concentration of Cu increases continuously can be given as it goes to the surface from an inside of Si powder.

[0017]** How to heat-treat at a suitable temperature and to make an inside diffuse a metallic element from the surface of an active material particle after forming a layer of Li and a metallic element which is not alloyed with a mechano-fusion method on the surface of Li and an active material particle to alloy.

[0018]When Cu is used as a metallic element, using Si grain as Li and an active material particle to alloy, Si powder and Cu particles are mixed mechanically, a Cu layer is formed on the surface of Si powder with a mechano-fusion method, it heat-treats at a temperature suitable after that, and Cu is diffused in Si powder, and concentration distribution which concentration of Cu increases continuously can be given as it goes to the surface from an inside of Si powder.

[0019]Although various methods can be considered according to the 2nd aspect of affairs of this invention as a method of manufacturing an active material particle in which concentration of Li and a metallic element which is not alloyed is decreasing as it goes to the surface from an inside of Li and an active material particle to alloy, the following methods are mentioned, for example.

[0020]** How to heat-treat at a suitable temperature after providing a layer of an active material alloyed with Li by electroless plating on the surface of Li and metal particles which are not alloyed. For example, when using Cu as Li and a metallic element which is not alloyed, using germanium as Li and an active material to alloy, it can produce by such a method.

[0021]** How to heat-treat at a suitable temperature after forming a layer of an active material alloyed with Li

with a mechano-fusion method on the surface of Li and metal particles which are not alloyed. When using Cu as Li and a metallic element which is not alloyed, using Si as Li and an active material to alloy, mix mechanically and Cu powder and Si grain with a mechano-fusion method. After forming a Si layer on Cu powder, it heat-treats at a suitable temperature and Si is diffused in Cu powder, and concentration distribution in which Cu is decreasing can be given as it goes to the surface from an inside of a particle.

[0022]** How to diffuse this returned active material in metal particles at the same time it returns this oxide at a suitable temperature in reducing atmosphere, such as a hydrogen air current, after forming a layer of an oxide of an active material with a mechano-fusion method etc. on the surface of Li and metal particles which are not alloyed.

[0023]When Cu is used as Li and a metallic element which is not alloyed, using Si as Li and an active material to alloy, a SiO layer or a SiO₂ layer is formed by mechano-fusion method or other methods on Cu powder, While making this oxide return at a suitable temperature in reducing atmospheres, such as a hydrogen air current, Si formed by reduction is diffused in a Cu particle, and concentration distribution in which concentration of Cu is decreasing can be given as it goes to the surface from an inside of particles.

[0024]Temperature of heat treatment for diffusing a metallic element in the above-mentioned ** - ** is an absolute temperature standard, and it is preferred that it is within the limits of about 1 / temperature raised from a room temperature about by ten to 4/5 of the melting point of metal to diffuse.

[0025]

[Embodiment of the Invention]Although this invention is hereafter explained still in detail based on an example, in the range which is not limited to the following examples at all and does not change the gist, it changes suitably and this invention can be carried out.

[0026][Production of this invention cell]

(Production of negative electrode active material) mean particle diameter -- one -- micrometer -- Si powder -- 100 -- g -- a table -- one -- being shown -- 35 -- ** -- solution -- 500 -- cc -- three -- a minute -- between -- having been immersed -- after -- rinsing -- ten -- volume -- % -- HCl -- solution -- five -- a minute -- between -- being immersed -- things -- Si powder -- the surface -- electroless plating -- a catalyst -- becoming -- Pd -- a core -- having formed .

[0027]

Table 1)

物質名	化学式	濃度
塩化パラジウム	$\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$	$0.2 \text{ g} \cdot \text{dm}^{-3}$
塩化第一銅	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	$15 \text{ g} \cdot \text{dm}^{-3}$
濃塩酸	HCl	$200 \text{ cm}^3 \cdot \text{dm}^{-3}$

[0028]Next, it was immersed in the electroless plating bath which adjusted this Si powder the pH to 12.5 of the presentation shown in Table 2 until the surface became Cu color. Thus, the Si powder in which the Cu layer was formed on the surface was heat-treated under a 500 ** vacuum, and Cu was diffused in Si powder.

[0029]

Table 2)

物質名	濃度
硫酸銅	$7.5 \text{ g} \cdot \text{dm}^{-3}$
ロッシェル塩	$85 \text{ g} \cdot \text{dm}^{-3}$
ホルムアルデヒド (3.7%)	$22 \text{ cm}^3 \cdot \text{dm}^{-3}$
安定剤 (メタノール)	7.5%

[0030]In order to check that Cu is spread in Si powder by the above-mentioned heat treatment, it checked by SIMS analysis that formed the Si film of 2 micrometers of thickness with the CVD method on Cu foil, heat-treated this instead of Si powder, and Cu was spread in a Si thin film. Drawing 1 is a figure showing this result. As shown in drawing 1, it turns out that Cu exists in a Si thin film and Cu is spread in a Si thin film. It turns out that it is increasing as Cu in a Si thin film goes to the surface from the inside of a Si thin film. Therefore, it turns out that it has the concentration distribution which the concentration of Cu increases as in the case of the above-mentioned Si powder Cu is spread in Si powder and it goes on the surface from an inside.

[0031][Production of a working pole] The negative electrode active material 100g produced above was mixed in N-methyl-pyrrolidone solution dissolved so that the fluoro-resin (PVdF) which is a binder might be 5%, stone mill was carried out with the stone milling machine for 30 minutes, and the slurry was produced. With the doctor blade method, it applied on 18-micrometer-thick electrolytic copper foil, it dried, and this slurry was started in size of 2x2 cm, and was made into the working pole.

[0032][Production of a counter electrode] 0.9-mm-thick Li metal was cut down in size of 3x3 cm, and it was considered as the counter electrode.

(Production of a test cell) After piling up the working pole and counter electrode which were produced above via the separator made from polypropylene, the glass plate was inserted, it was immersed into the electrolysis solution, and the test cell was produced. Li metal was immersed in the electrolysis solution so that these electrode groups might not be touched, and it was considered as the reference pole. As an electrolysis solution, what dissolved 1 mol/l. of LiPF₆ in the constant volume mixed solvent of ethylene carbonate and diethyl carbonate was used.

[0033][Production of a comparison cell] Except using Si powder 100g with a mean particle diameter of 1 micrometer as negative electrode active material as it is, the comparative study cell as well as the above-mentioned test cell was produced, and it was considered as the comparison cell A. silicification with a mean particle diameter of 1 micrometer -- except using the copper powder 100g as negative electrode active material as it is, the comparative study cell as well as the above-mentioned test cell was produced, and it was considered as the comparison cell B.

[0034][Charge-and-discharge cycle test] Charge was carried out to 0V on Li standard, discharge was carried out to 2V on Li standard, and the charge and discharge current did the charge-and-discharge cycle test of each above-mentioned test cell as 0.5 mA. The service capacity and charge and discharge efficiency of each test cell are shown in Table 3.

[0035]

[Table 3]

サイクル数	本発明電池		比較電池A		比較電池B	
	放電容量 mAh/g	充放電効率 %	放電容量 mAh/g	充放電効率 %	放電容量 mAh/g	充放電効率 %
1	2 0 0 0	9 1	6 4 0	2 1	6 1 0	4 8
2	1 9 9 0	9 9	3 2 0	5 0	4 5 0	7 4
5	1 9 5 0	9 8	1 5 0	8 2	3 5 0	8 7
10	1 8 8 0	9 7	1 3 0	8 2	2 9 5	8 7

[0036]As shown in Table 3, even if this invention cell piles up the number of cycles compared with the comparison cells A and B, it shows high service capacity and shows good charge and discharge efficiency. Although the negative electrode active material of a test cell had a little the portion which has exfoliated from the Cu foil which is a charge collector in this invention cell when the test cell after 10 cycles was decomposed, the negative electrode active material itself was maintaining shape. On the other hand, in the comparison cells A and B, negative electrode active material almost exfoliated from the charge collector, and the negative electrode active material itself did not maintain shape, but pulverization advanced, and, as for most, having distributed and dropped out in an electrolysis solution was checked.

[0037]As mentioned above, pulverization does not produce this invention cell by a charge-and-discharge cycle test, either, but the outstanding cycle characteristic is shown.

[0038]

[Effect of the Invention]According to this invention, the pulverization of an active material particle can be controlled and cycle performance can be raised by leaps and bounds.

[Translation done.]